

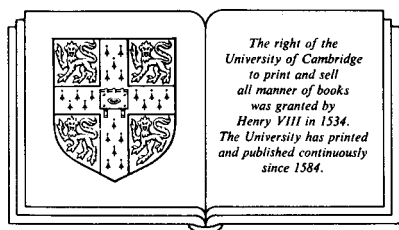
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# MOLECULAR COLLISIONS IN THE INTERSTELLAR MEDIUM

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# Interstellar molecules

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Molecules are extensively observed in our own and other galaxies, in objects such as planetary and cool stellar atmospheres and the interstellar medium. The molecules are observed through the emission or absorption of radiation at characteristic frequencies extending from the radio to the ultraviolet part of the electromagnetic spectrum. It is through the interpretation of this radiation that we learn about the astronomical objects that are responsible for its emission or absorption.

If radiation is emitted in conditions of thermodynamic equilibrium, a single parameter, the temperature, can be derived from spectral observations of the source. In fact, we observe distinct atomic and molecular species through their spectral lines, which are produced under conditions that may be far removed from thermodynamic equilibrium. In order to interpret these observations, it is necessary to know the rates of all the microscopic processes that determine the populations of the emitting or absorbing levels. An important category of these processes involves collisions between the molecules of the medium. The problem of calculating the rates of molecular collision processes is addressed in this monograph.

A first and rough indication of which molecules are likely to be abundant in astronomical objects is furnished by the cosmic abundances of the elements. The most abundant elements are listed in Table 1.1. Allowing for the fact that helium and neon are chemically inert, we would expect molecules bearing  $^1\text{H}$ ,  $^{12}\text{C}$ ,  $^{14}\text{N}$  and  $^{16}\text{O}$  to be amongst the most common. This expectation is amply confirmed by observations of the interstellar medium. It is the interstellar medium which is the subject of the ensuing discussion.

## 1.1 Formation of molecular hydrogen in the interstellar medium

In the interstellar gas, particle densities are low and atomic hydrogen exists predominantly in its 1s electronic ground state. Collisions

## 2 *Interstellar molecules*

between hydrogen atoms can then proceed along either of two potential energy curves, in which the electronic spins are either parallel (triplet state) or anti-parallel (singlet state). As the electronic orbital angular momenta are zero, the projection of this orbital angular momentum on the internuclear axis of the quasi-molecule that is formed is also zero, and the corresponding molecular states are denoted  $^3\Sigma$  and  $^1\Sigma$ . As is well known from the Heitler–London theory of the  $\text{H}_2$  molecule, the  $^1\Sigma$  state is attractive whilst the  $^3\Sigma$  state is repulsive. Fig. 1.1 illustrates the variation of these potential energy curves with internuclear distance,  $R$ .

As the atoms are initially unbound, their total energy,  $E$ , is positive. In order to stabilise, the system must lose energy and  $E$  become negative. In the gaseous phase, this may occur (a) through three-body collisions, the third body taking away the excess energy, or (b) through radiative processes. Even in the denser molecular clouds, three-body collisions are extremely improbable, and the only way in which the system can stabilise is through the emission of a photon. However, transitions between the  $^3\Sigma$  and  $^1\Sigma$  electronic potential energy curves are forbidden to electric dipole radiation as they involve a change in the total spin quantum number. Radiative transitions involving the nuclear degrees of freedom (rotation and vibration) are also forbidden, as the  $\text{H}_2$  molecule is homonuclear and does not possess a permanent dipole moment. It follows that the formation of  $\text{H}_2$  by two-body association in the gaseous phase cannot explain the observed presence of molecular hydrogen in the interstellar medium.

An alternative and, currently, the only viable theory of  $\text{H}_2$  formation

Table 1.1. *Relative number densities of the most cosmically abundant elements. With the exception of hydrogen, the number of neutrons in the most abundant isotope is equal to the atomic number. Data from Anders & Grevesse (1989)*

Element	Atomic number	Abundance
Hydrogen	1	10 000
Helium	2	1000
Carbon	6	4
Nitrogen	7	1
Oxygen	8	9
Neon	10	1

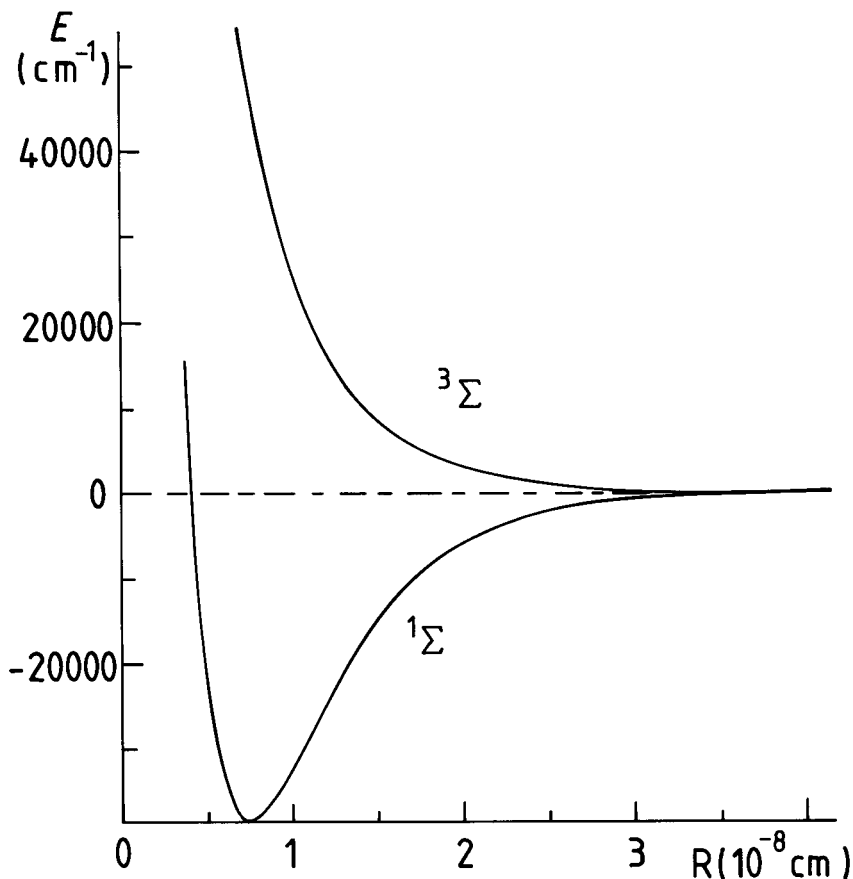


in interstellar clouds is through grain surface reactions (Hollenbach & Salpeter 1971). The grain acts as a catalyst, playing the rôle of the third body in a three-body reaction. Estimates of the rate of formation of  $\text{H}_2$  on grains (Hollenbach, Werner & Salpeter 1971) suggest that most of the hydrogen may be expected to be in molecular form in the dense molecular clouds.

In conditions where  $\text{H}_2$  is much more abundant than  $\text{H}$ , most of the collisional excitations of atoms and molecules will be induced by  $\text{H}_2$ . Helium atoms, which have a larger mass and lower mean speed at a given kinetic temperature, play a secondary rôle.

Molecular hydrogen can exist in two forms, or modifications, denoted

Fig. 1.1 Electronic potential energy curves correlating with  $\text{H}(1s) + \text{H}(1s)$  at large internuclear separation  $R$ . The notation is  $^{2S+1}\Lambda$ , where  $S = 0$  or  $1$  is the total electronic spin and  $\Lambda = 0$  is the projection of electronic orbital angular momentum on the internuclear axis.



ortho- and para- $\text{H}_2$ . In the former, the nuclear spins are aligned resulting in  $I = 1$ , whereas, in the latter, the spins are opposed and  $I = 0$ . As the nuclei are identical fermions, the nuclear wave function, which comprises vibration, rotation and spin components, must be asymmetric under exchange of the protons. The ground vibrational state function is invariant under this operation, whereas the rotational function is multiplied by  $(-1)^J$ , where  $J$  is the rotational quantum number. The triplet spin function,  $I = 1$ , is symmetric under proton exchange, and the singlet function,  $I = 0$ , is asymmetric. It follows that, in ortho- $\text{H}_2$  ( $I = 1$ ), only odd values of  $J$  are allowed, and in para- $\text{H}_2$  ( $I = 0$ ), only even values are allowed. In Table 1.2 are listed the energies of the first few rotational states of para- and ortho- $\text{H}_2$ .

In conditions of thermodynamic equilibrium, the relative abundance of ground state ortho- and para- $\text{H}_2$  is given by the Boltzmann relation,

$$n_1/n_0 = (\omega_1/\omega_0) \exp(-170.5/T), \quad (1.1)$$

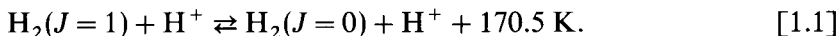
where  $T$  is the temperature. The ratio of statistical weights,  $\omega_1/\omega_0 = 9$ , is the ratio of values of  $(2I + 1)(2J + 1)$ . On the other hand, it is generally assumed that ortho- and para- $\text{H}_2$  are produced, on grains, at high temperatures, in the ratio of their nuclear spin statistical weights, that is, in a ortho:para ratio of 3:1. Subsequent radiative decay in the gaseous phase will preserve this ratio, leading, at low temperatures, to  $n_1/n_0 = 3$ . Whether this value or the thermodynamic equilibrium ratio (1.1) above is appropriate depends on the rate of interconversion of ortho- and para- $\text{H}_2$ .

In the low-temperature gaseous phase, the dominant reaction converting

Table 1.2. *Energies of the lowest few rotational states of para- and ortho- $\text{H}_2$ , expressed in kelvin ( $1 \text{ K} \equiv 0.695 \text{ cm}^{-1}$ ). Data from Jennings, Bragg & Brault (1984)*

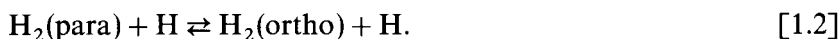
$J$			
para- $\text{H}_2$	ortho- $\text{H}_2$	$E_J(\text{K})$	
6		3475	
	5		2504
4		1682	
	3		1015
2		509.9	
	1		170.5
0		0	

ortho- to para- $\text{H}_2$  is expected to be proton exchange (Dalgarno, Black & Weisheit 1973):



If reaction [1.1] is rapid, then equation (1.1) will obtain. However, the rate of [1.1] depends on the proton density in the molecular cloud, which in turn depends on the rate of cosmic ray ionisation and on the chemistry. Detailed calculations (Flower & Watt 1984) have shown that the ortho:para abundance ratio varies from an initial value of 3:1 to the thermodynamic value on a time-scale which is a function of the chemical history of the cloud. In general, both ortho- and para- $\text{H}_2$  should be considered as possible collision partners in such media.

When a molecular cloud is subjected to heating and compression by a shock, an additional mechanism for converting para- to ortho- $\text{H}_2$  must be considered:



This reaction proceeds at a rate  $8 \times 10^{-11} \exp(-3900/T) \text{ cm}^3 \text{ s}^{-1}$  (Schofield 1967) and is sufficiently rapid that the ortho:para ratio in the hot postshock gas may differ significantly from the ratio in the cold ambient medium.

At the low temperatures and densities which prevail in the ambient medium, both ortho- and para- $\text{H}_2$  will be predominantly in their rovibrational ground states. In the case of para- $\text{H}_2$ , this state has zero rotational angular momentum ( $J=0$ ) and the corresponding rotational eigenfunction is the spherical harmonic  $Y_{00} = (4\pi)^{-1/2}$ . The implication of the eigenfunction being a constant, independent of the angles, is that all orientations of the internuclear axis are equally probable. The para- $\text{H}_2$  molecule then behaves similarly to the corresponding two-electron atom, that is, to helium. In particular, long-range interactions involving the permanent multipole moments of the molecule (of which the quadrupole is the leading term) vanish identically.

Many of the calculations of cross-sections for interstellar collision processes have been carried out with  $^4\text{He}$  as the collision partner, rather than  $\text{H}_2$ . The applicability of the results of these calculations to interstellar conditions resides on the analogy between interactions involving  $^4\text{He}$  and para- $\text{H}_2(J=0)$ . The mass difference between  $^4\text{He}$  and  $^1\text{H}_2$  may be taken into account when evaluating rate coefficients as averages of the corresponding cross-sections over a Maxwellian velocity distribution. It should be stressed that the analogy involves para- and not ortho- $\text{H}_2$ , which may, in fact, be more abundant. Long-range interactions with the permanent multipole moments of  $\text{H}_2$  do not vanish in the case of ortho- $\text{H}_2$  and can

lead to substantial differences in the rates of transitions induced by ortho- and para- $\text{H}_2$  at low temperatures.

## 1.2 Formation of molecules more complex than $\text{H}_2$ in the interstellar medium

It is not our intention to enter into a discussion of the involved and sometimes contested theories of heavy molecule formation in the interstellar medium. The interested reader should refer instead to a specialised text, such as the book of Duley & Williams (1984). We shall restrict our attention to those aspects of the theory, relating to the formation of the simpler molecules, which have gained general acceptance. Our aim is to establish the categories of collision processes that are likely to be important.

Most specialists would agree on the relevance of ion–neutral reactions to the formation of interstellar molecules. In the context of the dense molecular clouds, such reactions were first discussed in detail by Herbst & Klemperer (1973). The long-range attraction, due to the polarisation of the molecule by the ion, ensures that these reactions are generally rapid at the low temperatures of the ambient medium, providing they are exothermic. In shocked molecular gas, the latter restriction no longer applies owing to the higher kinetic temperature and, in magnetohydrodynamic shocks, to ion–neutral streaming (ambipolar diffusion).

In dense molecular clouds, cosmic ray (CR) ionisation of molecular hydrogen is expected to be the primary ionisation process,



followed rapidly by



which yields an  $\text{H}_3^+$  ion. Heavier molecules may then be produced through a sequence of ion–neutral and dissociative recombination reactions,



followed by



or



and



Production of the hydroxyl radical and the water molecule is possible by this sequence of reactions. A similar sequence, initiated by



generates carbon-bearing species. It should be noted that dissociative recombination reactions, such as [1.7] and [1.9], are generally rapid owing to the long-range Coulomb attraction between the reactants involved and the low mass of the electron, which ensure a high collision frequency.

In diffuse clouds, where atomic hydrogen is more abundant, the primary ionisation process



assumes importance. The proton that is produced may undergo charge exchange with atomic oxygen,



although this reaction is slightly endothermic. Charge transfer processes are very important in the interstellar medium and are considered in Chapter 6. A hydrogen abstraction reaction,



then initiates the same sequences as [1.5] above. Chemical fractionation may also occur through an alternative process of charge transfer with deuterium,



followed by



which is exothermic, owing to the difference in the zero-point energies of  $\text{H}_2$  and  $\text{HD}$  and, to a lesser degree, in the ionisation potentials of  $\text{H}$  and  $\text{D}$ . Chemical fractionation, in this example, the enrichment of the medium in  $\text{HD}$ , occurs because reaction [1.15] is exothermic whereas the analogous reaction involving  $\text{H}^+$  has a zero energy defect. More significant, in practice, is the reaction



which can yield high degrees of deuteration of  $\text{H}_3^+$  (Watson 1976).

In regions that have undergone shock heating, endothermic reactions and those with barriers less than a few thousand kelvin must also be taken into account. The energy required to drive these reactions derives from the thermal motion of the reactants in the hot gas, or, in the case of magnetohydrodynamic shocks, from the relative streaming of the ionic and

neutral fluids (ambipolar diffusion). In particular, the endothermic reaction



becomes effective in producing  $\text{CH}^+$ , which had, for many years, resisted all attempts at explaining its observed abundance in the diffuse interstellar medium (cf. Dalgarno 1976). The possibility that some species must be selectively produced in shocked regions of molecular clouds has been a major stimulus to work on interstellar chemistry in recent years. The interrelationship between shocks and chemical processes is considered in Chapter 7.

The rate of an endothermic reaction or a reaction with a barrier has an exponential dependence on the temperature of the medium in which the reaction occurs. It follows that collisional processes affecting the thermal balance of the gas can be of critical importance in determining its chemical composition. In Chapter 2, we discuss rotational excitation processes, which intervene in the thermal balance of both the cold ambient medium and the hot shocked gas. Vibrational excitation assumes importance in hot media and is discussed in Chapter 3. The excitation of fine structure transitions in atoms and ions, which plays a rôle in the thermal balance of the interstellar gas, is considered in Chapter 4. Selective excitation mechanisms, which can lead to population inversion and maser action, are illustrated by reference to the OH radical in Chapter 5.